

Fly ash as the component of composites materials

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The fly ash from powerplant can be compared, due to its genesis, chemical and mineralogical composition with the natural volcanic glasses and minerals generated in the process of devitrification in situ. Its quality is comparable to non-metallic aluminosilicate raw materials that are commercially used in building and ceramic industry. Two possibilities of fly ash utilization as the most bulk waste produced by anthropogenic activity were examined.

The way of fly ashes utilization in the modeling of mixtures for the high refractory mullite corundum materials synthesis was examined. In this experiment 95.5% conversion of the input components of fly ash and Al additive in the ratio 1:1 on the mullite and corundum was obtained.

Keywords: black coal fly ash, mullitization, technolithes.

INTRODUCTION

Increase of the technogenous wastes content exceeds the auto regeneration ability of the nature. Exhausting of the primary raw materials and wastes production has reached the critical level, and it is necessary to include the wastes of useful components content in the raw materials cycle. This is the aspect of the new interdisciplinary geosciences-technical branches of research that are known as material engineering and technolithology¹.

Technolithology is especially focused on the geosciences-technical area and also works on adding the wastes to the earth's material cycle in the form of the newly produced composites and technolithes². Many of the technolithes have their natural equivalents. One of the examples are fly ashes that are similar, because of their genesis and composition, to the volcanic ashes and from them created the aluminosilicate minerals. It is therefore anticipated that also the areas of their utilization could be similar and in technologies could partially substitute raw materials. The basic characteristics which allow including the examined fly ashes in the earth's material cycle are connected, particularly with the possibility of fly ashes Si-Al matrix utilization for the refractory technolithes development.

The results from the research on the rational fly ashes from the heating plant TEKNO inc. Kosice, Slovakia, utilization focused on its application by developing the new type of refractory technolithe of mullite-corundum type, were presented.

In nature mullite is created in the zones rich in Al, above all in the sillimanite, andalusite, cyanite and topaz form, as a result of its contact with high temperatures of lava streams. The temperature of thermal transformation of the mentioned aluminosilicates to mullite is around 1300°C³. Also other aluminosilicates should be transformed to mullite, e. g. talc⁴⁻⁶ but only in the suitable stoichiometric ratio of Al and Si that is 3:2⁷⁻⁹. Industrially the bulk of the mullite production comes from kaolinite and synthetic Al₂O₃. The composition of the commercially used refractory materials produced and used in industry is practically never of mono-mineral composition. In table 1 examples of the commercially produced refractory materials are shown¹⁰.

Following the data shown in table 1 it is evident that for the new technolithes on the fly ash basis creation the content of Al₂O₃ and the ratio of the majority components of technolithe, Al₂O₃ and SiO₂ are important. The second important factor is the process of thermal transformation of mullite and corundum.

Table 1. Commercially produced refractory materials, raw materials, mineral compositions and the areas of their utilization, after Gregerova¹⁰

Refractory technolithes	Mineral composition of base crude	Mineral composition of technolithe	Abundance of basic oxides	Temperature resistance - utilization
Silica chamotte	kaoline, claystone, clay, quartz sand	mullite, cristobalite, tridymite, quartz	10-30% Al ₂ O ₃	up to 1670°C
Clay chamotte	Refractory clays, claystones	mullite	35-45% Al ₂ O ₃	up to 1750°C
High clayey chamotte	Refractory clays, claystones, hydroxides and oxides, Al minerals Al ₂ SiO ₅	mullite, cristobalite, corundum	45-60% Al ₂ O ₃ 60-75% Al ₂ O ₃ over 75 % Al ₂ O ₃	up to 1840°C up to 1900°C up to 1950°C
Mullite refractory technolithes	Al hydroxides and oxides, sillimanite, andalusite, cyanide	mullite, cristobalite, corundum	60-85% Al ₂ O ₃	up to 1960°C
Examined waste fly ash	Black coal with accessory rocks	amorphous vitric phases Si-Al, quartz, cristobalite, mullite, corundum, feldspars, unburned coal, hematite, maghemite, graphite, montmorillonite, tobermorite, hydrargillite-gibbsite ⁶	Al ₂ O ₃ 20.86 % SiO ₂ 47.10 %	As refractory material inapplicable without pretreatment!

MATERIALS AND METHODS

Fly ash

Black coal fly ash from the heating plant TEKOS Kosice without treatment, of the chemical composition shown in table 2, was examined.

From the XRD analysis of the fly ash sample it was found that the dominant phase in the fly ash is the amorphous vitric phase. Then the minerals such as: quartz, cristobalite, anhydrite, feldspar, corundum, magnetite, hematite and graphite were identified.

Thermal properties of the examined fly ash are as follows: by 1230°C softening, by 1270°C thawing and over 1270°C fluxing.

Al additive

As Al additive (G) pure $\text{Al}(\text{OH})_3$ – gibbsite (hydrargillite) with the content of Al_2O_3 65.3% and H_2O 34.7% was used. Gibbsite is changed during the thermal treatment at 196–202°C to boehmite $\text{AlO}(\text{OH})$, at 950°C is disintegrated and creates $\gamma\text{-Al}_2\text{O}_3$ ⁴.

The composite mixtures preparation was focused on 3 different mixing ratios of the fly ash and gibbsite (ratios 2:1, 1.5:1 and 1:1). With these ratios the similar stoichiometric ratios of Al_2O_3 and SiO_2 similar to mullite were anticipated. The mixtures of both components were consequently homogenized in the planetary mill for 10 minutes. The prepared mixtures products were thermally modified by the temperatures of 850, 1050 and 1500°C. The obtained new materials were thereafter analyzed for the mullite and corundum components that are the basic for the refractory materials.

The process of thermal transformation by 0, 850, 1050 and 1500°C was evaluated by XRD analysis. The inert standard-pure ZnO (c. 5 weight %) was added to the process of mullitization with the aim to quantify the amorphous components and the new-produced phases in the composite mixtures. The samples were homogenised with this standard by micro-milling and consequently boxed up in the glass cuvette.

The measurement was provided by the full automatic diffraction meter URD-6 (Rich Seifert-FPM, Germany) under the following conditions: emission of $\text{CoK}\alpha/\text{Ni}$ rejecter, potential of 40kV, ampere of 35 mA, step mode $0.05^\circ 2\theta$ with the step time of 3s and the digital processing of the measured data. For the measuring and results evaluation software RayfleX (RayfleX ScanX and RayfleX Analyze, 2.289 version) was used.

RESULTS AND DISCUSSION

With regard to the phases composition, the elementary qualitative-quantitative parameters of the prepared composite materials are shown in table 4 and in figures 1–3. The results of the thermal transformation of basic fly ash components are shown in table 3. As a result of the temperature influence, the content of the amorphous phases of the fly ash decreased. There was a momentary

decrease of mullite contents at the temperature of the 850°C, thereupon the metastable corundum structures were formed. However, with the increase of the temperature to 1050°C, the mullite content increased to the double value of the original sample. The total content of the refractory components increased to 1050°C. At higher temperatures the treated sample was totally melted and devaluated.

In table 4 and figures 1–3 the experimental results of the thermal transformation of composite mixtures of the fly ash and gibbsite milled for 10 minutes in the planetary mill, are presented. The temperature influence and the mixing ratio of the fly ash and gibbsite on the mullite corundum phases creation in the newly prepared technolites was monitored.

The course of the phases changes by the thermal processing of the composite mixtures of the fly ash and gibbsite in the 2:1, 1.5:1, 1:1 mixing ratios are shown in figures 1–3.

Following the comparison of the results showed in table 4 and figures 1–3, it is possible to say that at 850°C in all

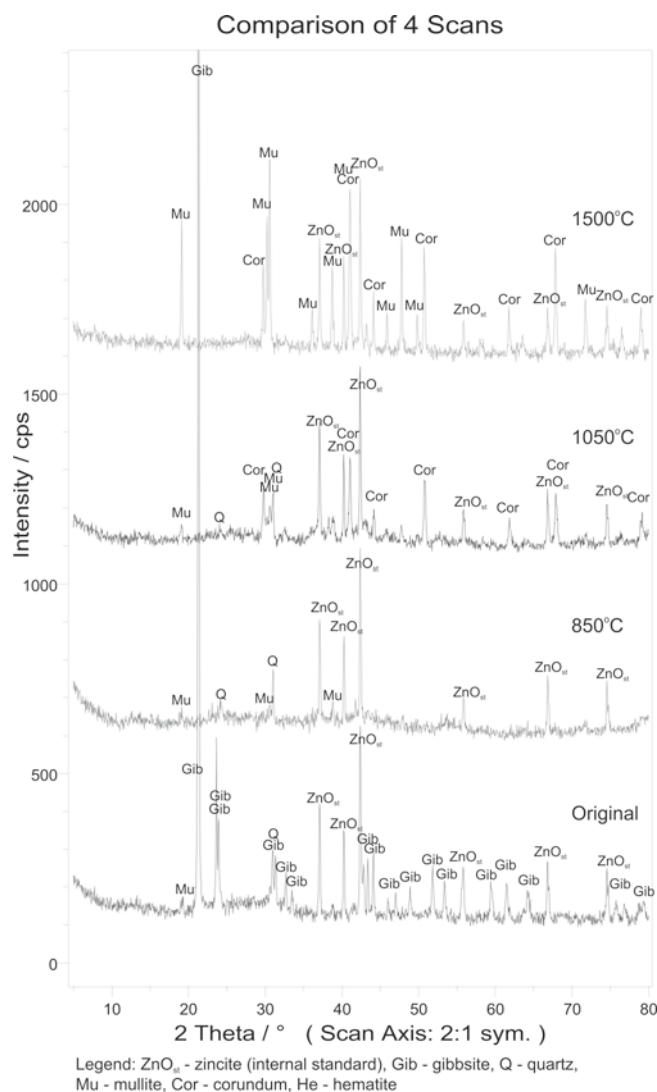


Figure 1. Phases changes by the thermal processing of the composite mixture in the ratio 1:1

Table 2. Chemical composition of examined fly ash (P)

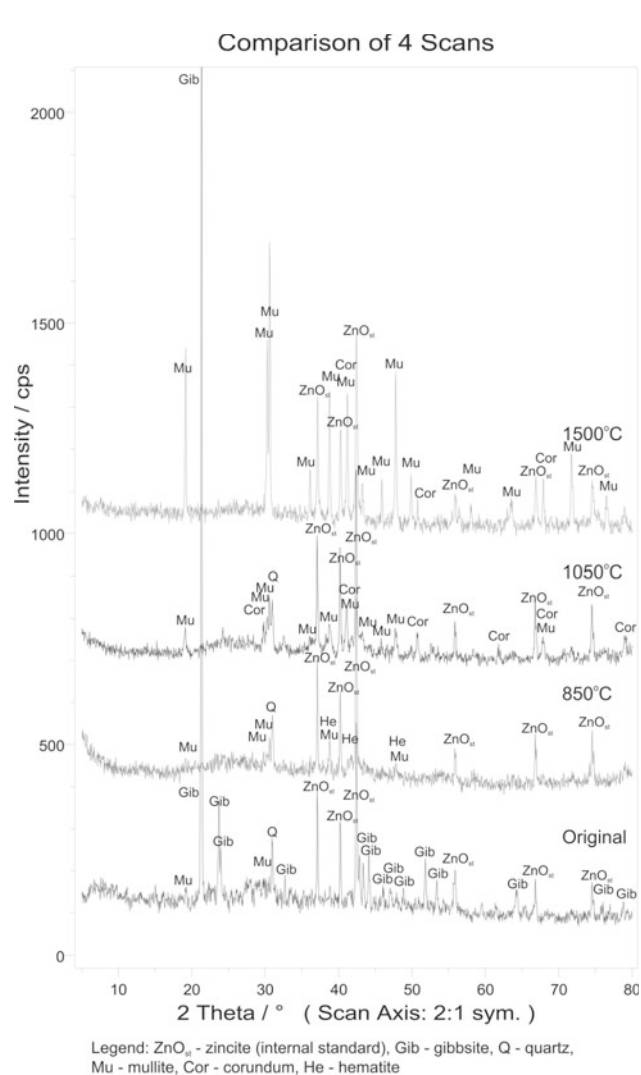
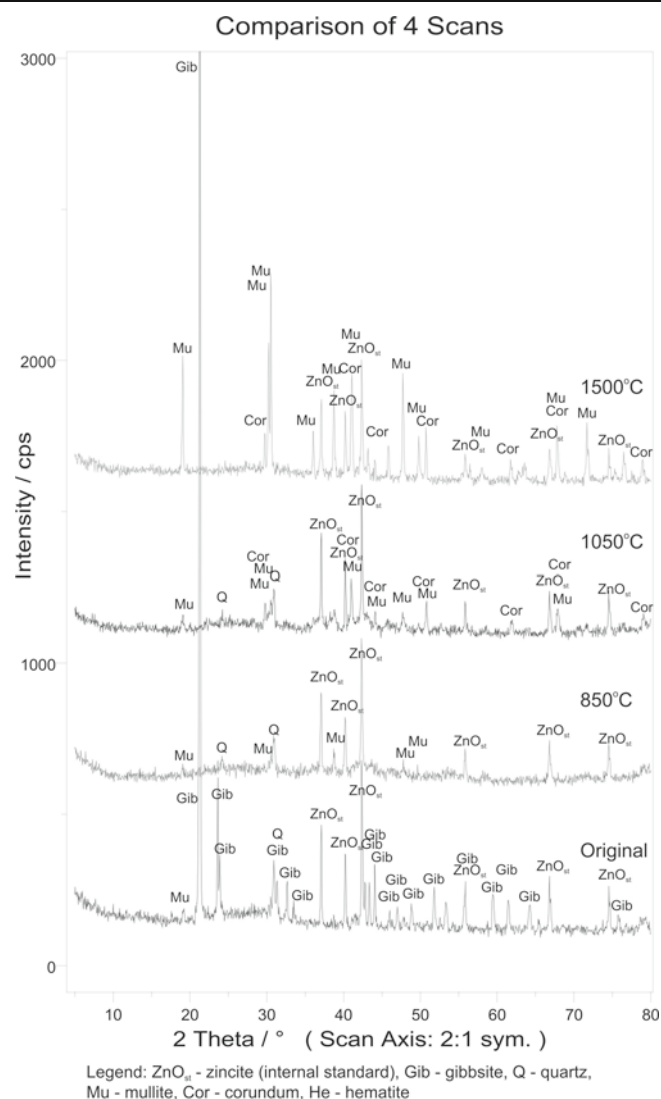
Annealing lost (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	TiO_2 (%)	MgO (%)	Na_2O_3 (%)	K_2O (%)	P_2O_5 (%)	S_{total} (%)	pH
15.5	47.10	20.86	8.83	23.80	0.76	1.21	0.78	2.14	0.35	0.15	12.4

Table 3. The influence of thermal transformation on the phase's composition of examined fly ash

Mixing ratio P : G	Transformation temperature (°C)	Content (%)			
		Amorphous phases	Mullite	Corundum	Refractory material
1:0	0	83.05	10.66	–	10.66
	850	72.3	9.29	2.96	12.25
	1050	64.3	22.7	–	22.7
	1500	Sample was melted and devaluated			

Table 4. The qualitative-quantitative composition of prepared technolites of mullite-corundum type

Mixing ratio P : G	Transformation temperature (°C)	Content (%)				
		Amorphous phases	Mullite	Corundum	Refractory material	Al ₂ O ₃
2 : 1	0	50.5	6.79	–	6.79	
	850	86.2	4.82	0.85	5.67	
	1050	69.2	14.54	7.45	21.99	
	1500	39.8	56.8	2.35	59.15	35.60
1.5 : 1	0	37.4	4.61	–	4.61	
	850	88.95	3.84	0.54	4.38	
	1050	63.0	14.3	13.3	27.6	
	1500	21.5	63.8	13.3	77.1	40.01
1 : 1	0	30.0	5.4	–	5.4	
	850	86.58	3.96	1.44	5.4	
	1050	54.0	12.7	23.9	36.6	
	1500	2.1	59.0	38.9	97.9	43.13

**Figure 2.** Phases changes by the thermal processing of the composite mixture in the ratio 2:1**Figure 3.** Phases changes by the thermal processing of the composite mixture in the ratio 1.5:1

the experiments a sharp increase of the amorphous phases content and in the content of refractory components in the case of the gibbsite dehydration was noted. With the continual increase of the temperature, the content of the refractory components rose from 6.79% to 20–36.6% at 1050°C up to 59–97.5% at 1500°C.

During the mullite phases creation there was the optimal fly ash and gibbsite ratio of 1.5:1, where at 1500°C the technolite of 63.8% mullite content was prepared.

During the corundum phases creation with the optimal conditions in the 1:1 ratio and the temperature of 1500°C, the maximal corundum content of 38.9% was achieved. Under the same conditions the maximal sum of both refractory components in the prepared technolithe, namely 97.9%, was obtained.

With respect to the commercial categorization of the refractory materials and its Al_2O_3 content (see table 4) it is possible to integrate the prepared technolithes to the category of “normal chamotte” of 1750°C refractoriness.

CONCLUSION

The presented results confirmed that the examined black coal fly ashes are wrongly classified as waste. The possibility of its effective usage by the preparation of new materials and technolithes that have good household properties has been confirmed. This is only one of the examples of the possible way of the examined fly ash utilization. In industrial production fly ashes should substitute part of the primary raw materials with the positive impact on the economics and environment. This is only the question of the focused research to find the most suitable application of this waste material by creating the new composite materials and technolithes.

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